Title	Studies on the α, β-Transformation of Glycosides. (II) : The Transformation of β-ethylglucoside
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concentration.

Potato phosphorylase was prepared from 3 l. potato juice by repeated fractional precipitation with ammonium sulfate. The final fraction was 1.105—1.125 in specific gravity. The phosphorylase obtained proved to have almost no ability of starch formation when no activator was added.

20 g. of potato starch was boiled in 100 cc. of 1% H_2SO_4 for 20 minutes; then H_2SO_4 was removed with $BaCO_3$. The filtered solution was concentrated to a thick syrup under reduced pressure and dried in a vacuum desiccator. 10 g. of the product (polysaccharide mixture) was extracted with each 100 cc. of 90, 80, 60, 40 and 20% ethanol successively and finally with water under reflux condenser. The chain length of the polysaccharides thus prepared were 1.5, 2.9, 5.0, 8.0, 10.8 and 42.2 glucose units respectively (as calculated on the determination of reducing power).

It is concluded that, among these polysaccharides, the fraction of 5.0 glucose units shows the highest activating ability while the natural starch, such as sweet potato, rice and glutinous rice, and synthetic starch prepared in our laboratory (Inouye, Onodera and Kisaki, Rep. Inst. Chem. Res. Kyoto Univ., **18**, 39 (1949)) show lower activating ability than their hydrolyzed products.

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71. Studies on the α, β-Transformation of Glycosides. (II)

The Transformation of β-ethylglucoside.

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In the previous paper (Rep. Inst. Chem. Res. Kyoto Univ., **18**, 37 (1949)) it was reported that β-methylglucoside is transformed to α-methyl-glucoside by means of $SbCl_5$ which is found to be more convenient than $SnCl_4$ (E. Pacsu, Ber., 61, 137 (1928)) or $TiCl_4$ (Ber., 61, 1508 (1928); J. Am. Chem. Soc., 52, 2563 (1930)). Recently B. Lindberg (C. A., **43**, 3785 (1949)) reported on the transformation of β-glucosides to α-form by means of BF_3. The present paper is a report on the transformation of β-ethylglucoside to α-form catalyzed by $SbCl_5$.

Tetraacetyl-β-ethylglucoside (m. p. 106—107°, $[\alpha]_D^{20}$ −22.7° ($CHCl_3$); E. Fischer, Ber., **49**, 584 (1916)) was dissolved in purified chloroform (alcohol-free), and $SbCl_5$ dissolved in chloroform was added. After a definite time, the chloroform layer was shaken with distilled water, treated with a small amount of $BaCO_3$ and filtered. The filtrate was dried, filtered, and then concentrated to a thick syrup under a reduced pressure, a small amount of abs. ethanol was added and cooled with ice for several hours. The β-form which was not transformed was crystallized out and filtered off. After addition of a small amount of dist.

water, the filtrate was allowed to stand for 5 days and the crystal of α-form deposited. This was filtered off and recrystallized from abs. ethanol.

Several cases of the experiments are shown in the following table.

					α-form		
β-form	$SbCl_5$ (in 5 cc $CHCl_3$)	$CHCl_3$	Temp.	Time	Yield	m. p.	$[\alpha]_D$
1 g	1 cc	8.6 cc	0^0	30 min.	0.07 g	57^0	$[\alpha]_D^{18}$ 140^0
1	1	8.6	0	20	0.08	58	$[\alpha]_D^{13}$ 136.3
1	1	8.6	10	30	0.14	58	$[\alpha]_D^{17.5}$ 138

From the result of the be experiments carried out under various conditions it is concluded that the optimum reaction temperature seems to be 10^0, at 20^0 the reaction product is destroyed, and at 0^0 the reaction is too slow.

The crystal obtained proved to be α-ethylglucoside by observing the specific rotation and the melting point, and gave no depression of the melting point when mixed with the specimen prepared after Ferguson (J. Am. Chem. Soc., **54**, 4086 (1932)).